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GEOMETRIC ISOMERS OF 2-NAPHTHYLPHENYLCARBENE: A REVISED ASSIGNMENT

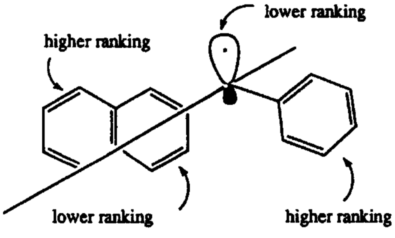
HEINZ D. ROTH*
Wright-Rieman Laboratories, Rutgers University, New Brunswick, New Jersey 08855-0939, USA
AND
MATTHEW S. PLATZ*
Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA

It is reported that earlier assignments of 2-naphthylphenylcarbene were erroneous and that ESR data support the same assignment as quantum mechanical calculations. An unambiguous nomenclature for geometric isomers of carbenes is proposed.

1. INTRODUCTION

Recent quantum mechanical calculations on 2-naphthylphenylcarbene (NPC) using *ab initio* and semi-empirical methods[1] confirmed the previously reported existence of two different geometrical conformers;[2] the results led to the conclusion that the conformer with the lower ground-state triplet energy and the lower triplet–triplet (T_0–T_1) transition has the larger zero-field splitting (zfs) parameter, $|D/hc|$. This assignment is contrary to an earlier ESR study, in which the two rotamers with $|D/hc| = 0{\cdot}3898\ \mathrm{cm}^{-1}$, $|E/hc| = 0{\cdot}0195\ \mathrm{cm}^{-1}$ and $|D/hc| = 0{\cdot}4044\ \mathrm{cm}^{-1}$, $|E/hc| = 0{\cdot}0168\ \mathrm{cm}^{-1}$ (in a frozen THF matrix) were identified based on a qualitative evaluation of the π-electron spin density in NPC.[2] We report here that the assignments in the earlier paper were erroneous; the ESR data support exactly the same assignment as the quantum mechanical calculations. We also note an ambiguity in the *designation* of the carbene isomers and propose an unambiguous nomenclature for geometric isomers of carbenes.

In a series of publications on geometric isomerism in divalent carbon species,[3–7] the carbene isomers were designated as '*cis*' and '*trans*' based essentially on an evaluation of the 'substituents' according to the sequence rules. Several singlet carbenes, recognized on the basis of their electronic absorption spectra and assigned with the help of *ab initio* calculations, were designated similarly.[8,9] On the other hand, the isomers of some carbenes with larger aryl substituents have been designated according to a *syn*–*anti* convention, where the species having the singly occupied sigma orbital next to the larger fragment of the major substituent was designated the *syn*-isomer.[2] Given the precedent of the earlier publications and the potential for ambiguity, we propose an unambiguous nomenclature for divalent-carbon isomers (rotamers), in which the 'substituents' at the bond between the divalent carbon and the non-symmetrical substituent are ranked based on the sequence rules, viz.,



E-NPC

Carbenes bearing two non-symmetrical substituents require two stereochemical indicators describing the relative arrangement of substituents around the two bonds linking the divalent carbon to the non-symmetri-

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[*] Authors to whom correspondence should be addressed.

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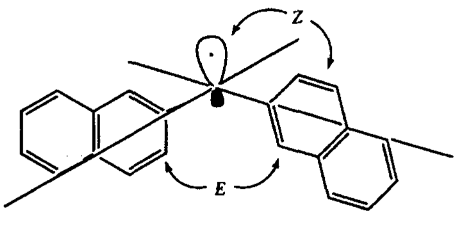
cal substituents, as illustrated for the *Z,E*-isomer of bis-2-naphthylcarbene[(*Z,E*)-bis-2-NC].



Z, E-bis-2-NC

Because of the importance of the correct assignment for the proper understanding of geometric isomerism in triplet (and singlet) carbenes, we briefly rehearse the simple qualitative analysis of electron spin densities underlying the assignment of the isomers. Triplet carbenes have two unpaired electrons, a σ-electron essentially localized at the divalent carbon, and a π-electron which is delocalized throughout the π-system. It has been noted[3,4] that the zero-field splitting (zfs) parameter, $|D/hc|$ of such a species can be reproduced by a point spin model,[10] with individual contributions, D_i, due to π spin densities, ρ_i, at individual carbon atoms, C_i, viz.,

$$D_i \propto \rho_i\left\langle\frac{r_i^2-3z_i^2}{r_i^5}\right\rangle \approx \rho_i\left\langle\frac{1}{r_i^3}\right\rangle \qquad (1)$$

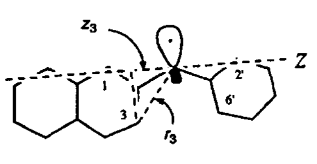
where r_i is the distance between the divalent carbon, C_{di}, and a carbon, C_i, bearing π spin density, and z_i is the z coordinate of C_i. According to equation (1), contributions to $|D/hc|$ fall off with $1/r_i^3$. Thus, the magnitude of $|D/hc|$ is determined primarily by the π-spin density at the divalent carbon, ρ_{di};[3,4] the zfs observed for NPC, $|D/hc| \approx 0{\cdot}4\ \mathrm{cm}^{-1}$, corresponds to a spin density $\rho_{di} \approx 0{\cdot}55$. Carbenes with delocalized spin density will have noticeable secondary contributions to $|D/hc|$ due to the nearest carbons with π electron spin densities; for NPC, these include carbons C-2′, C-6′ of the benzene ring and C-1 and C-3 of the naphthalene system, respectively. The contributions due to the spin density on benzene are identical for both isomers; those due to spin density on the naphthalene system are significantly different.

For the *E*-isomer, C-1 lies close to the z-axis so that r is approximately parallel to z. Hence, $z_1 \approx r_1$, and

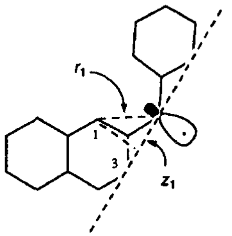
$$D_1 \approx \rho_1\left\langle\frac{r_1^2-3z_1^2}{r_1^5}\right\rangle \approx \rho_1\left\langle\frac{-2z_1^2}{r_1^5}\right\rangle \approx \rho_1\left\langle\frac{-2}{r_1^3}\right\rangle \qquad (2)$$

causing a noticeable negative contribution to $|D/hc|$. The π electron density at C-3 makes a lesser contribution, because $\rho_3 \approx \frac{1}{2}\rho_1$, and because C-3 is far from the z-axis; accordingly, $z_3 < r_3$. Simple geometric considerations suggest that the angle between the r_3 and z_3 vectors lies close to 55°; correspondingly, $r_3^2 - 3z_3^2 \approx 0$.

A similar inspection of the *Z*-isomer shows that C-3 lies close to the z-axis ($z_3 = r_3$), whereas C-1 is far from the z-axis ($z_1 > r_1$). Accordingly, the contributions due to the spin densities at C-1 and C-3 are interchanged, and the negative contribution to $|D/hc|$ is smaller since it is caused by the center bearing lesser spin density, $\rho_3 \approx \frac{1}{2}\rho_1$. These considerations clearly suggest that the *E*-conformer must have the smaller $|D/hc|$ value. Hence, the isomer with $|D/hc| = 0{\cdot}3898\ \mathrm{cm}^{-1}$ must be the *E*-isomer and that with $|D/hc| = 0{\cdot}4044\ \mathrm{cm}^{-1}$ must be the *Z*-isomer. The previous analysis[2] recognized correctly that the *E*-isomer has the larger secondary contribution, but failed to take into account the negative sign.



E-NPC



Z-NPC

In summary, we emphasize that the rotational isomers of carbenes can be assigned readily from a simple *inspection* of the 'nearest' spin densities, as long as these are clearly understood. It may be sufficient to compare the nearest spin densities close to the z-axes of the two isomers [i.e., ρ_1 for (*E*)-NPC, ρ_3 for (Z)-NPC], since contributions due to spin densities far from the z-axes are significantly smaller.

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